CHEMICALS FROM BIOLOGICAL RESOURCES

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by ALAN J. P. DALTON

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INTRODUCTION

This survey represents an attempt to stimulate those people surrounded by abundant, and renewable natural resources to see them as raw chemical materials; which, by simple processing often suitable for cottage industries, may enable them to overcome some of their other economic and social needs.

The survey makes no attempt at being comprehensive,(although I would be grateful for details of serious omissions). Many of the common biological resources (e.g. cocoa) have been omitted, since they are too well known to be included. However, where certain important alternative 'chemical' uses exist they are given (e.g. Sugar).

Many of these processes are no longer operated in highly industrialised societies, since other resources (e.g. coal, petroleum, natural gas; non-renewable incidentally), or their frequent labour intensive requirements, have made them uneconomic. Although it is impossible to judge the "economic feasibility" of many of these processes out of their "operating environment" and the particular country/area needs, the following points may be relevant:

1) Many of the resources are renewed in a fairly short life-span (1-10 years).

2) They are often labour, as opposed to capital, intensive.

3) Many processes use only "waste" by-products of normal production.

4) Many of the processes are based on "pre-industrial" techniques and hence can often be converted to the conditions of developing countries more readily than more modern processes.

The economic viability can be viewed from roughly three positions:

(a) Production is for local use (e.g. dyes for fabrics etc.) where economic viability is self-evident.

(b) Production is for internal use in the country of origin; where import data and prices can (hopefully) be obtained for a rough costing.

(c) Production is for export; the situation here is far more complex, since it is not only economics but the problem of breaking into established

markets which must be considered. It is best to consult external expert advice with regard to export (e.g. The Tropical Products Institute, London, do excellent, if pessimistic, surveys on potential markets for products; prepared at the request of under-developed nations, and the International Trade Centre, Geneva, Switzerland).

Although many biological resources have the advantage of being renewed in a fairly short life-span, such a renewal carries with it the disadvantage that such resources are more susceptible to over exploitation and rapid ecological damage (e.g. the "dust bowls" created by over-farming). It is therefore imperative that environmental scientists are consulted <u>before</u> operating any of these processes, so that the possible consequences to the environment can be estimated; and monitoring set up to detect any environmental deterioration.

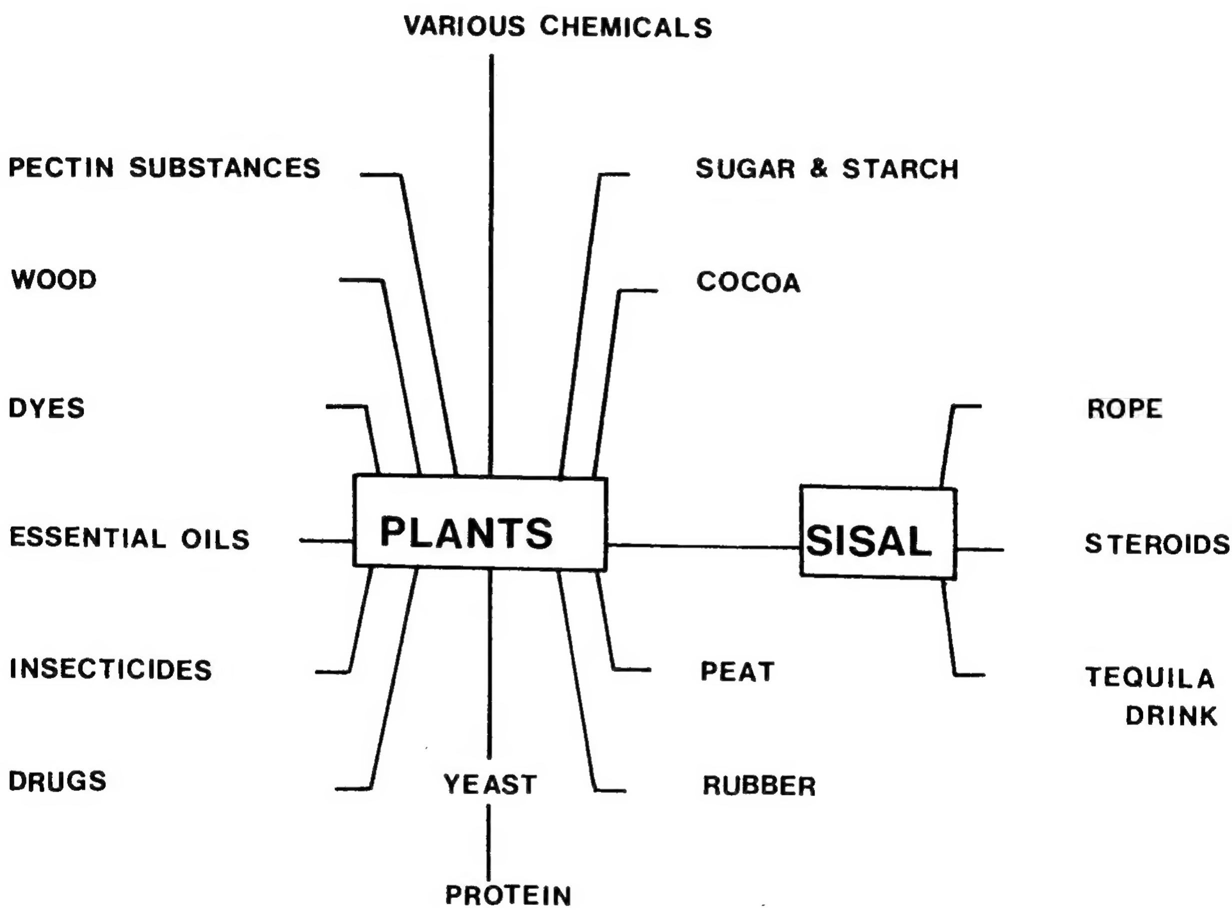
This first general survey will be followed by a series of more detailed reports at two distinct, but overlapping, levels:-

(i) A detailed survey, including economic prospects for export and references, etc., of the various processes available for producing chemicals or chemical-like products, from a particular biological resource.

(ii) Fullest possible details of the <u>practical</u> operation for a <u>specific</u> process for the production of chemicals from a biological resource. It is expected that these reports will be prepared in response to requests from the proposed users of such a process.

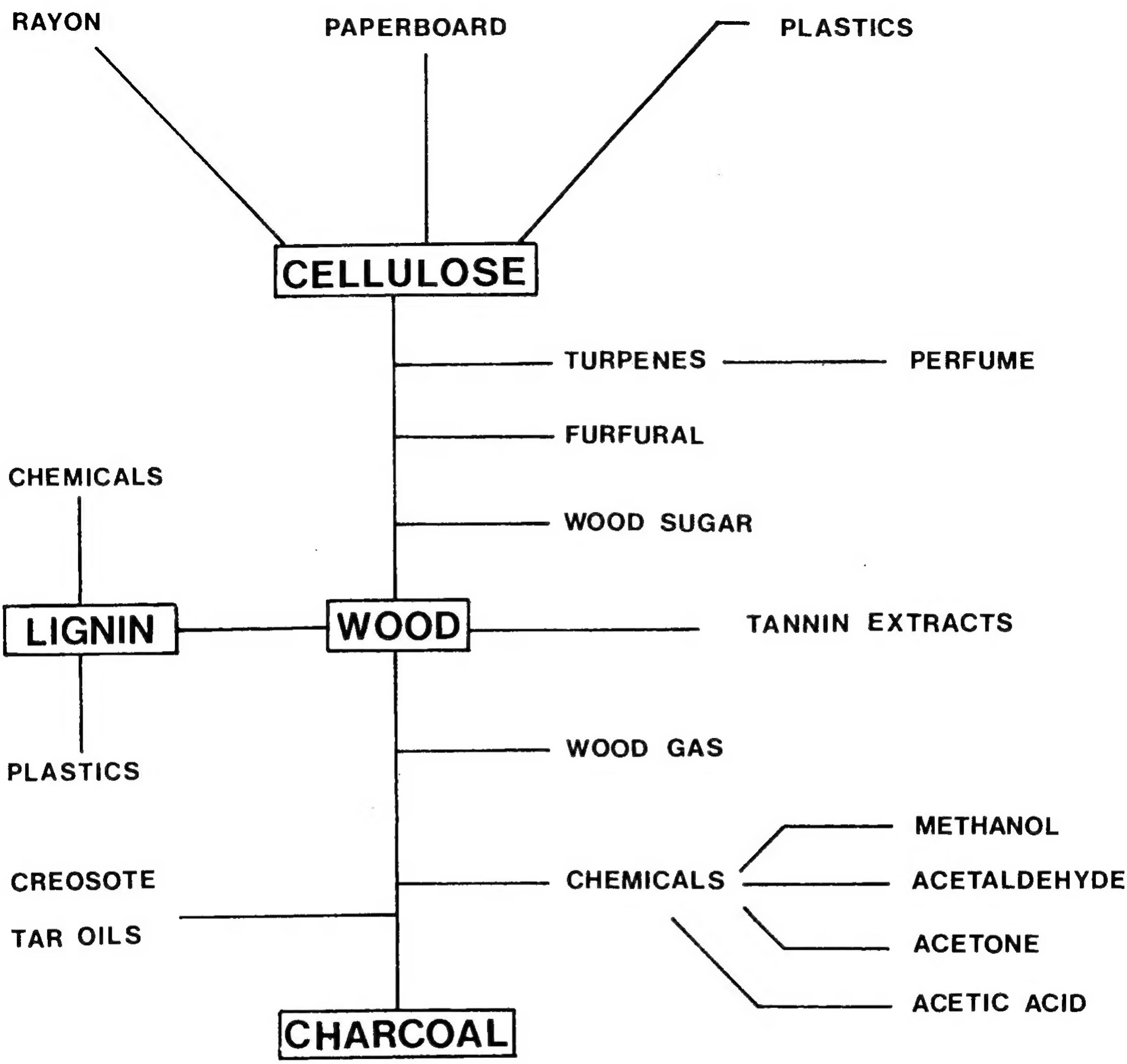
PLANT PRODUCTS

This is the major section of the report since many chemicals are obtained from plant resources. Ideally it would be desirable to combine intrinsic usefulness (e.g. as a building material, source of protein etc.) with by-product utility.



WOOD

Until the late 19th century, and the development of the coal-tar industries, wood was the major source of man's organic chemicals. Although currently wood is assuming decreasing importance in industrialised countries it is still one of man's most important natural resources. And, with the increasingly rapid rate of depletion of non-renewable resources, such as coal, oil and natural gas, wood may well regain some of its old importance.



The major constituents of wood are cellulose (60-80%) and Lignin (20-30%). The uses of the former are well known and outlined in the above diagram.

By comparison Lignin has received little attention yet the following low molecular weight chemicals are readily available from Lignin:

LOW MOLECULAR WEIGHT CHEMICALS	USE
Vanillin and derivatives	Flavouring and synthetic intermediate. (3$ lb. in 1960's; estimated world consumption in 1970's 9 million lbs.)
Methyl Mercaptan	Production of amino-acid Methionine - used as animal food supplement.
Dimethyl Sulphide	Conversion to Dimethyl Sulphoxide - a very useful solvent.
Acetic, Formic and Oxalic Acids.	General Chemicals
Tar Oil and Turpentine	" "
Various Phenols	" "

By modification of the polymeric nature of lignin the high molecular weight properties may be used to produce:

- Oil-well drilling muds
- Cement and concrete additives
- Dispersants
- Ore Flotation products
- Emulsifiers and Stablisers
- Grinding aids
- Products used in electrolytic refining
- Binders and adhesives
- Rubber additives
- Tanning agents
- Plastics

The uses of WOOD SUGAR are less well known and exploited. Treatment of wood chips/sawdust with dilute acid, under pressure, produces wood sugars in 45-50% yields.

Wood sugar has been used to obtain the following chemicals:

Glycerol	Lactic Acid
Oxalic Acid	Butyric "
2,3 - Butylene glycol	Acetic "
Furfural	

By fermentation alcohol and yeast have been obtained, e.g.

100 lb dry wood chips or sawdust ⟶ 2.5 gall. 100% alcohol
4 lb. dry yeast

Further wood sugar molasses give an acceptable livestock feed.

Finally there is dry distillation the process which once supplied the major chemicals of the world, the process is indicated in the following table:

PRODUCTS OBTAINED BY DRY-DISTILLATION OF 1 TON OF HARDWOOD SCRAP (ca. 70% MAPLE, 25% BIRCH 5% ASH, ELM AND OAK

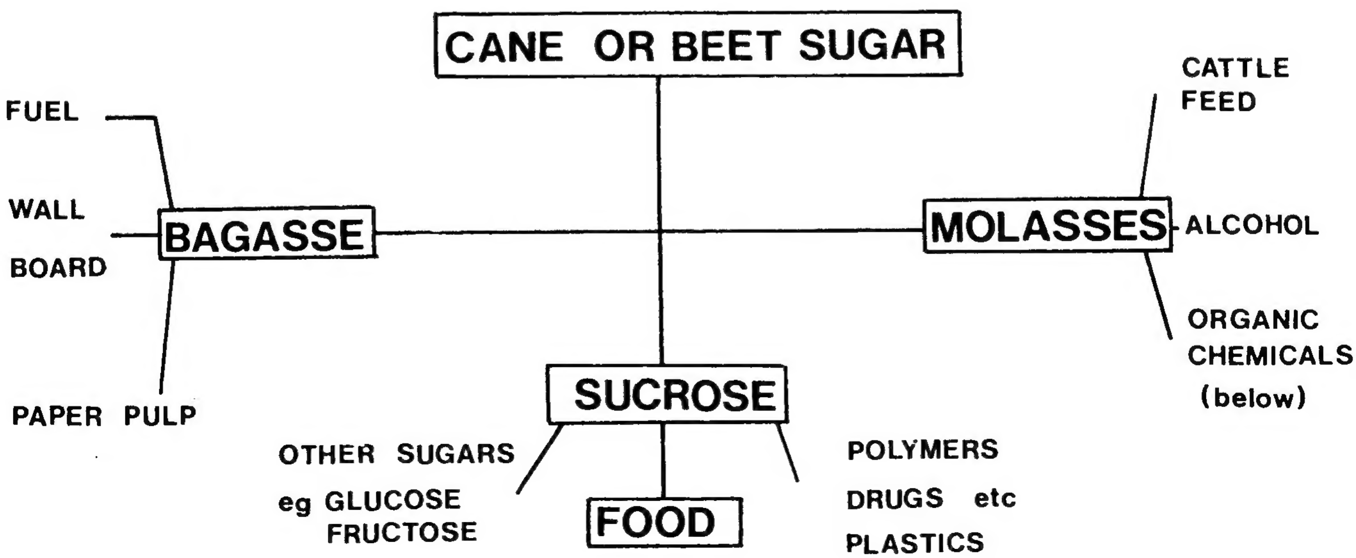
Charcoal	600 lb.
GASES:	5,000 cu.ft.
Carbon Dioxide (38%)	
Carbon Monoxide (23%)	
Methane (17%)	
Nitrogen (16%)	
Methanol	3 gall.
Ethyl Acetate	15 gall.
Ethyl Formate	1.3 gall.
Acetone	0.7 gall.
Creosote Oil	33 gall.
Sol. Tar	22 gall.
Pitch	66 lb.

TANNIN extraction is quite a simple procedure, and although quebracho is the most important source, the following table indicates other sources are important.

TANNIN CONTENT OF SOME PLANT MATERIALS

PLANT MATERIALS	% TANNIN
Chestnut wood	4-15
Hemlock bark	10-20
Tanbark oak	15-16
Chestnut oak	10-14
Black oak	8-12
Sumac leaves	25-32
Quebracho heartwood	20-30
Mangrove bark	15-42
Wattle (acacia bark)	15-50
Myrobalan nuts	30-40
Sicilian sumac leaves	25-30

SUGAR



Sugars may be obtained from cane or beet, but although the collection is labour intensive, the work is very hard and socially undesirable.

The major use of sugar is still as a food and the major aspects of the industry are well known, e.g. 1 ton Bagasse is approximately equal to 1 barrel of fuel oil.

However some of the other by-products have not received the attention they deserve and some of their uses are outlined below.

Fermentation of MOLASSES (or sulphite liquor from wood production, waste liquors from fruit and vegetable production, stillage waste liquors after alcohol and citric acid production) with the yeast Torulopsis utilis (candida utilis) yields protein with a high vitamin content, whose nutritional value appears to approach that of beef protein.

It has been estimated that, using fermenters and processes operating at high concentrations of wort and yeasts, with effective mechanical air distributors requiring low energy, and automatic feeding and control equipment, a compact plant built on several acres may well supplement the nourishment of 10 million people. The conversion of raw material to a finished high-grade protein can be done in 24 hours.

Molasses have also yielded the following common, and useful, organic chemicals:

Amino Acids	Acetic Acid
Acetone	Butyric "
Butanol	Lactic "
Glycerine	Citric "

Sugar (sucrose) itself is one of the most abundant pure raw organic materials.

The major alternative uses of sugar have been centred around plastics (especially bio-degradable) surfactants and surface coating agents; although many look promising no large-scale commercial use has yet been found.

Semi-commercial processes exist for the preparation of the following from sugar:

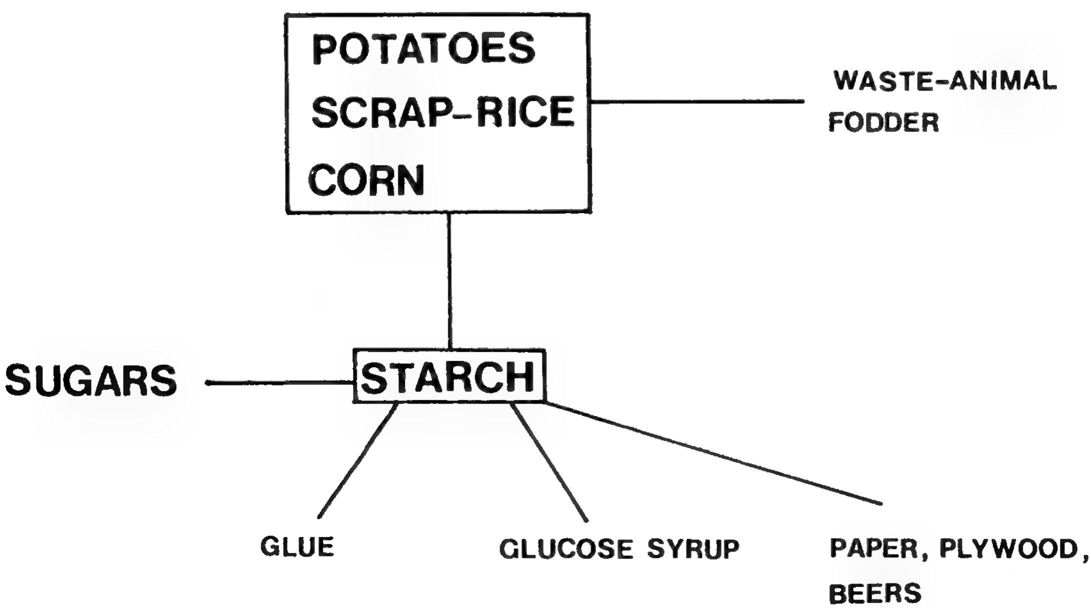
SUCROSE ESTERS
e.g. octaacetate-polymer
octobenzoate-plasticizer
sterate-biodegradable surfactant
SORBITOL
MANNITOL
D-GLUCONIC ACID
(riboflavine; vitamin B_2)
1-AMINO SORBITOL
TETRAHYDROPYRIDAZINES
2-METHYL-3-INDOLE ACETIC ACID
LEVULINIC ACID

HYDROXYMETHYLFURFURAL
ANGELICA LACTONE
2-METHYLPIPERIZINE
4-METHYLIMIDAZOLE
OXALIC ACID
MUCIC "
LACTIC "

In addition to the compounds mentioned under molasses we can also obtain, by fermentation, ethanol, fructose and raffinose.

A useful by-product of sugar cane is wax (ca.45% myricyl alcohol and other esters) which finds uses in polishes, varnishes and as a possible source for sterols.

STARCH



Starch is the most abundant reserve material in the vegetable kingdom. Much of it is hydrolysed to yield various sugars especially dextrose (D-glucose).

The following chemicals have been obtained from starch:

Sorbitol
gluconic acid
gluoheptonic acid
methyl glucoside

NATURAL DYES

Although most of the natural dyes of antiquity have now little or no commercial use in modern industry, some are still in use in home industries and by handicraft workers. To this day, some of the natural dyes and pigments, e.g. Logwood, osage orange and Bitumen, retain most of their old importance.

The following table illustrates some of the more important natural dyes:

COLOUR	COMMON NAME	OCCURANCE	DYEING USE
YELLOW	Dyers Rocket	Reseda Luteola L	Wool dyeing - best fast yellow
"	-	Curcuma longa	Cotton, wool, silk
"	-	Extract of safflower corella	Colouring of objects
"	Jaffron	Crocus sativus L (Iris)	Textiles Food dye
"	Osage orange	Maclura pornifera	Wool, nylon, silk, leather
ORANGE	Annatto	Bixa orellana L	Cotton, wool, silk, foodstuffs & printing
RED	Cochineal	Coccus cacti L (Insect)	Wool, Food-stuffs
"	Barwood Camwood Sanderswood Narrawood	Baphia nitida and Pterocarpus aanalinus L	Wool, cotton, Chrome leather and foodstuffs
"	Brazin	various species of Caesalpina	Cotton, wool, leather and biological staining
"	Dyer's Thistle	Carthamus tinctorius L	Textiles, flowers, food, cosmetics & pigments.
BLUE	Indigo	various Indigofera	Textiles

(Contd.)

BROWN	Venetian Sumach	<u>Rhus cotinus L</u>	Textiles Leather
BLACK	Logwood	-	Most fabrics

<u>INSECTICIDES</u>

These are normally the dried root or leaves of the plant or simple extracts of the same. Although often very complex substances, mixtures are usually satisfactory.

The major ones are:

COMMON NAME	SOURCE	USE
<u>NICOTINOIDS</u>	<u>Nicotinaria tobacum</u> <u>N. rustica</u> <u>Duboisia hopwodii</u> <u>Aesclepias syrisca</u> 2-15%	Contact insecticide for aphids. Fumigants for green-houses & poultry mites.
<u>PYRETHROIDS</u>	<u>Chrysanthemum cineraiifolium</u> <u>C. coccineum</u> (0.7 - 3%)	General purpose. esp. aerosols etc.
<u>ROTENOIDS</u>	<u>Tephrosia</u> <u>Derris</u> <u>Lorichocarpus</u> <u>Milletia</u> <u>Mundulea</u> 10-25% total extractives	Application to edible products prior to harvest. Control of animal ecto-parasites & cattle grub
<u>RYANIA</u>	<u>Ryana speciosa</u> family of <u>Flacourtiaceae</u> (0.16 - 0.2%)	More stable than pyrethum and rote-nones to light Shows promise vers. European cork-borer and other crop pests

Other plants used as insecticides include SABADILLA and CEVADINE; the latter has been used for the control of plant feeding Hemiptera and as a toxic bait for Thripps.

OILS, FATS, WAXES AND COSMETICS

Only the USA and USSR are self-sufficient in oils and fats, in general there is a heavy importation of fats and oil seeds by the industrialised nations from the agricultural and less industrialised countries.

The preliminary separation of the oil from the plant, etc. frequently involves just cleaning, crushing and cold-pressing (or solvent extraction). Further purification depends on the grades required.

The following tables indicate the major aspects of the industry.

The major sources of oils and fats are:

PLANTS	60%
ANIMAL	36%
MARINE	4%

OIL OR FAT	WORLD PRODUCTION (1962) (billions/lbs)	CONSUMPTION USA (1963) (1,000,000/ lbs)	AVERAGE WHOLESALE PRICE (¢ /lb. 1963)
Butter	8.70	-	58
Lard	8.36	800	8.2
Soybean	8.22	3,800	9.2
Tallow greases	7.55	2,200	8.2 4.8
Peanut Oil	5.10	70	12.6
Cottonseed	4.89	1200	10.1
Sunflower Oil	14.34	60	20.0
Coconut Oil	4.28	800	11.2
Olive Oil	2.89	-	54.7
Rupeseed Oil	2.84	-	13.4
Palm Oil	2.80	55	14.0
Linseed Oil	2.07	400	12.7
Tung Oil	-	44	42.2
Cod-liver Oil	-	-	16.9

Imports of WAXES in the U.S.A. in 1969 were 11.5 million/lb. valued at 3.67 million $. The major waxes imported are broken down in the following table, and their uses indicated also.

U.S.A. IMPORTS (1969)

WAX	AMOUNT 1000/lb	VALUE 1000 $
Beeswax	4,400	3,250
Carnauba	11,000	3,500
Montan	3,500	580
General Animal	520	370
Candelilla	3,250	1,560
General Vegetable	410	120

GENERAL USES OF WAX

Paper Coating

Candles

Textiles and leather sizing

Cosmetics and Pharmaceuticals

Greases

The essential OIL and COSMETIC industries are closely related. Many agricultural countries supply the industrialised countries with their requirements for essential oils, and there are signs of a revival in the use of natural products in cosmetics, as opposed to synthetics.

The important essential oils are found in the following table, and the following list gives the major natural products of interest to the cosmetic industry.

IMPORTANT ESSENTIAL OILS

NAME	METHOD OF PRODUCTION	PART OF PLANT USED
BAY	Steam	Leaves
CASSIA	"	Leaves and twigs
CEDARWOOD	"	Red core wood
CINNAMON	"	Bark
CITRONELLA	"	Grass
CLOVE	"	Buds
EUCALYPTUS	"	Leaves
GERANIUM	"	"
JASMINE	Cold pomade	Flowers
PEPPERMINT	Steam	Leaves and tops
ROSE	Steam, solvent, enfleurage	Flowers
SANDALWOOD	Steam	Wood
SPEARMINT	"	Leaves

MAJOR PLANT PRODUCTS OF INTEREST IN COSMETICS

OILS	FRUITS	HERBS
COCONUT	LEMON	ALOE
COCOA BUTTER	LIME	BIRCH
MINK	STRAWBERRY	COMFREY
HONEY ('BEE OIL')	CARROT	BURDOCH
ALMOND	CELERY	ST. JOHNS WORT OIL
TURTLE	PINEAPPLE	CHAMOMILE
SOY BEAN		CALENDULA (Marigold)
CUCUMBER		MISTLETOE
AVOCADO		YARROW
		BALSAM
		ALOE VERA

CORK

Cork is obtained from the bark of the cork oak, *Quercus suber*. When the tree is about 20 years old the cork is stripped, and after this may be stripped every 8 - 10 years. The bark is boiled with water, scraped and dried. Cork finds extensive uses in linoleum, insulation and it is highly resistant to corrosion. The market appears to be expanding and many industrialised countries import large amounts. (e.g. the U.S.A. imported ca. 60,000 tons in 1965).

DRUGS

Until the mid 19th century, and the birth of synthetic organic chemistry, plants were the only source of drugs for man. Although synthetics have replaced many plant drugs, some still retain their old importance, often due to their complexity. (Notable *recent* examples being the steroids and prostaglandins).

MAJOR DRUGS OBTAINED FROM PLANTS

PLANT	DRUG	USE
Dioscorea (Yams)	Steroids	Birth control
Soybeans	Diosgenin Stigmasterol	Anti-inflammatory etc.
Cinchona bark	Quinine	Malaria
Foxglove	Digitalis	Heart stimulant
Curare	Tubocurarine	Muscle relaxant
Ipeccac Root	Emetine	Amoebic dysentary
Autumn Crocus	Colchicine	Gout, Botany
Vinca Rosea Periwinkle	Vinblastine Vincrustine	Cancer
Rauwolfia Trees (Snakeroot)	Reserpine	Mental illness

PECTIN SUBSTANCES

Pectin is one of the most important polysaccharides in the food industry. Its application continues to expand and world production is in the region of 10,000 tons per annum.

The chief raw materials used in the production of pectin are by-products of the manufacture of apple or citrus juices, although sugar beet pulp has been used commercially for the recovery of pectic materials.

MAJOR SOURCES OF PECTIN

SOURCE	PECTIN (%)
Pirie Cambium	16.6
Lemon Rind	32.0
Lemon pulp	25.0
Turnip	10.0
Sugar beet pulp	30.0
Pineapple peel	20.0
Pineapple orange membrane	29.0

USES OF PECTIN

Foodstuffs (Jellys etc.)

Pharmaceuticals

Source of Pectic Enzymes

Clarification of fruit juices and wines

Retting

Wood preservation

PEAT

Various peats contain up to 22% wax, although 3-14% is more common. Although the extraction is not economic in industrialised countries, except at times of acute shortages of waxes from other sources (e.g. war), it should be viable in developing countries.

One of the most promising uses of peat appears to be as a source of protein. Hydrolysis of the carb-hydrates present in peat, combined with the other nutrients present in peat, forms a fermentable broth which supports the growth of Candida utilis; and there is little doubt about the high biological value of this protein. Although only at a preliminary stage, this process looks promising.

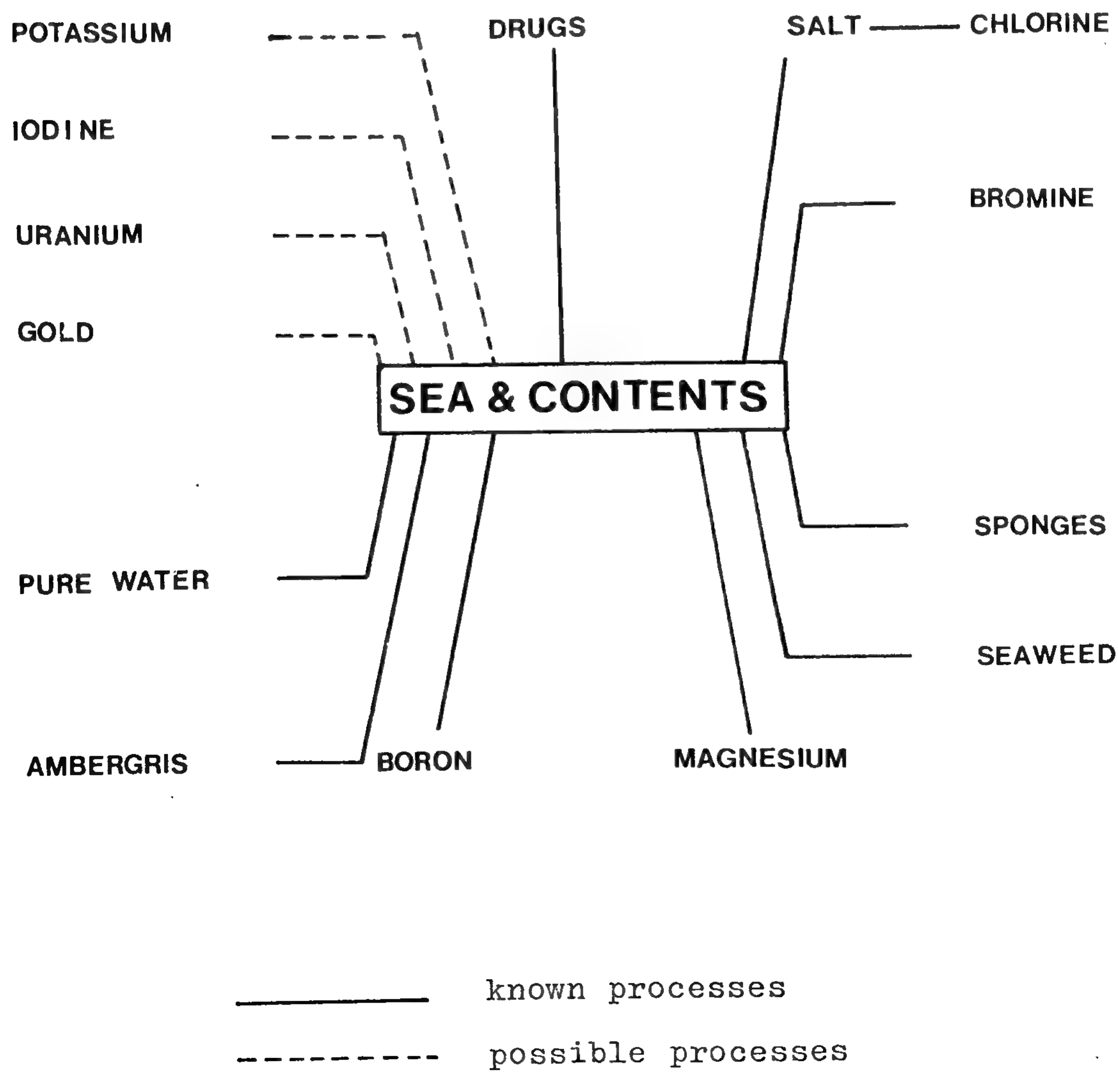
Besides the well known use of peat as a fuel and in agriculture, peat can contain up to 50% organic chemicals. ("Humic acids"). However, it appears that such chemicals which are present can be more readily obtained from wood sources.

MARINE PRODUCTS

Apart from a few industries (e.g. Fishing and Seaweed) marine resources have hardly been touched, when compared with the more readily available land resources.

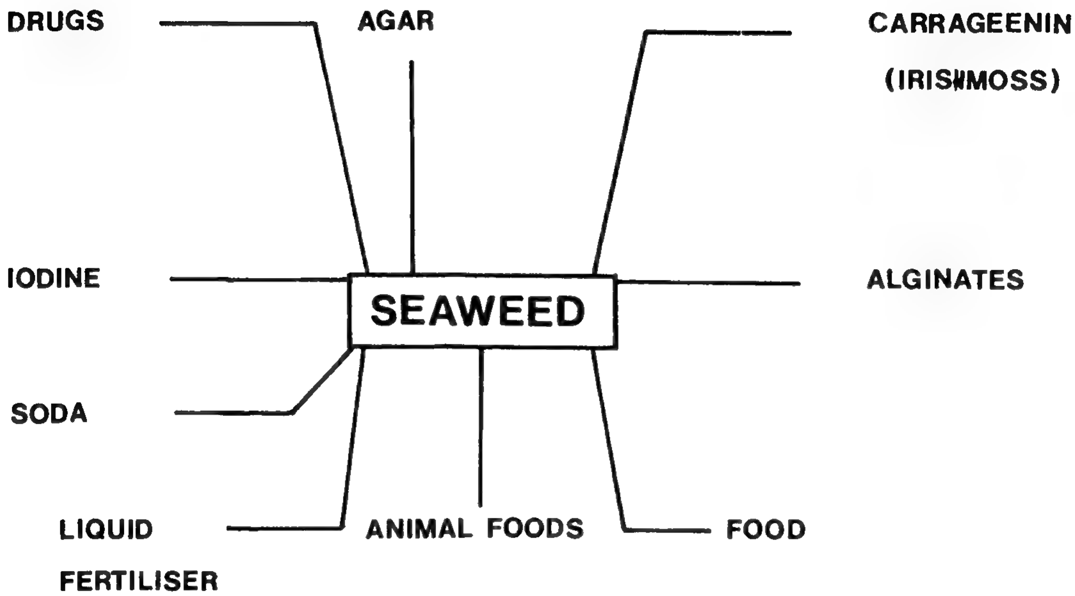
However preliminary methods exist for the extraction of many products and, with the increasing scarcity of land resources, consideration of the ocean as a source of raw materials will no doubt increase.

In consideration of the use of this untapped source, it is important that we learn from our mistakes on land, and ensure that any exploitation of these resources is done with the fullest possible regard to the ecological consequences.

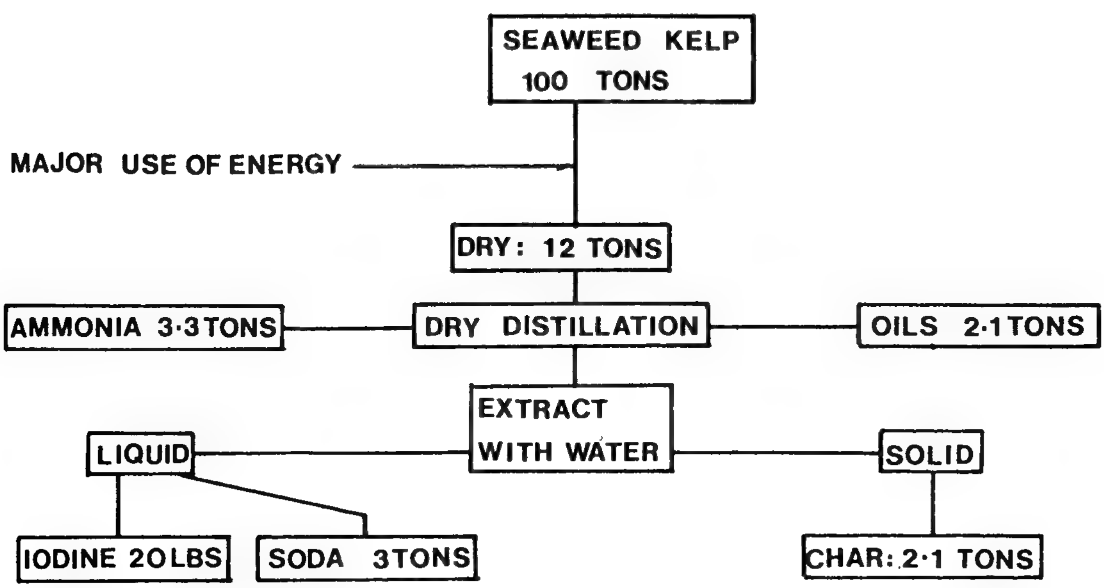


SEAWEED

Seaweed is regenerated every 4 years. Many of the older products of the industry (e.g. iodine and soda production) can no longer compete in the industrialised nations, but may be of interest in developing countries The demand for the more modern products of the industry (e.g. Alginates and Agar) appears to be increasing.



THE MANUFACTURE OF SODA AND IODINE



The three modern major products of the industry are indicated below, together with their uses.

PRODUCT	USES
Agar	Microbiology Foodstuffs Pharmaceuticals
Alginates	Pharmaceuticals Foods Rubber Textiles Paper
Carrageenin	Largely Foodstuffs Ceramics Alcoholic drinks Electroplating Leather finishing

In addition to these products, the sugars: Ducoidin, L-fucose, D-glucose, Laminarin and the steroid Fucosterol have been produced on a semi-technical scale.

<u>CHEMICALS POTENTIALLY AVAILABLE PER ANNUM</u>

<u>FROM 1,000 TONS OF FRESH 'L.CLOUSTINI' (Whole Plant)</u>

CHEMICAL	CALCULATED TONNAGE PRESENT IN WEED		
	MAY	OCTOBER	AVERAGE
Alginic Acid	28	31	30
Mannitol	10	33	18
Laminarin	Nil	40	14
Fucoidin	6	9	7.5

MINERALS

The major chemicals produced from seawater, as a by-product of salt production, are magnesium and potassium.

The following table illustrates the chemicals currently extracted from the sea:

CHEMICAL	CONCn. (mg/l)	Total Amount Present in Seawater (tons)	Reserves at todays consumption (millions years)	Value of Chemical in a ton Seawater (\$)
Sodium Chloride	29,500	45.6×10^{15}	+ 1,000	0.31
Magnesium	1,350	2.1 x "	"	1.00
Sulphur	885	1.4 x "	200	0.03
Potassium Chloride	760	1.2 x "	300	0.024
Bromine	65	100×10^{12}	1,000	0.02

Thus, the bulk of todays bromine is extracted from the sea. However, since much of the bromine produced is used to make petrol additives, which are urgently being reduced, the value of this product may decline, unless other uses are found.

Schemes have been devised to extract gold, uranium, iodine and potassium from seawater, but at the present time it is cheaper for industrialised countries to produce these from other sources.

DRUGS

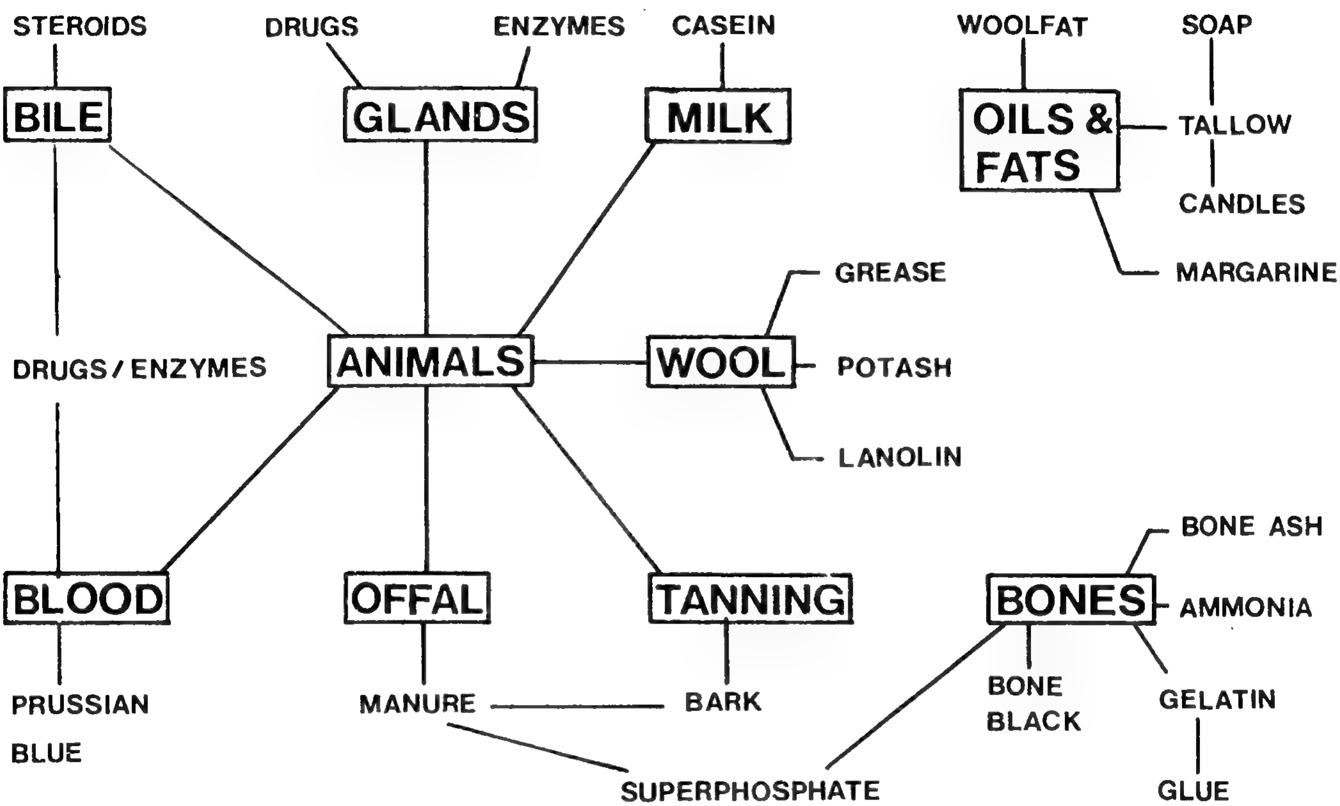
Many useful drugs are currently obtained from the sea, and many more are currently under investigation, some of those in current use are illustrated in the following table:

CURRENTLY USED DRUGS FROM THE SEA

DRUG	SOURCE	USE
Sodium Morrhuate	Cod Livers	Treatment of varicose veins
Cephalosporin C.	<u>C. Acremonium</u> (fungus)	Antibiotic
Kainic Acid	<u>Digeria Simplex</u> (Alga)	Anthelmiritic
Nereistoxin	<u>Lumbricinereis heteropa</u> (Sea Worm)	Insecticide
Tetrodotoxin	<u>Spheroides Spengleri</u> (Puffer fish)	Relaxes muscle spasms etc.
Prostaglandin	<u>P. Homomalla</u> (gorgonian soft coral)	Birth Control etc. etc.

ANIMAL PRODUCTS

Generally these will occur as "waste" products of food production.



Many of the uses of animal by-products are covered in other sections of this report (e.g. oils and fats) or are self-explanatory (e.g. bone ash etc.). The major exceptions are noted below.

DRUGS AND ENZYMES

Generally to obtain the final drugs, in the high state of purification required, takes some considerable sophistication. However, crude preparations are often easily prepared and frequently have considerable

value. Enzymes for industrial, as opposed to drug, use may not be required so pure, and there are signs that the use of enzymes, by industry, is rapidly increasing.

MAJOR DRUGS AND ENZYMES ISOLATED FROM ANIMAL SOURCES

ANIMAL SOURCE	DRUG (TYPE)	USE
Pancreas	Insulin (hormone)	Diabetes mellitus
"	Glucagon (hormone)	Antihypoglycerinic Agent
"	Pancreatin (enzyme)	Replacement therapy. Tanning.
Mammalian Tissue	Heparin (mucopolysaccharide)	Anticoagulant
Bile	Bile Acids (Steroids)	Anti-inflammatories Gall-stone dissolution
Spinal Chord of cattle	Cholesterol (Steroids)	Various
Gastric juice	Pepsin (enzyme)	Digestive-aids
Cartilagenous tissue, e.g. trachea, aorta, tendons, etc.	Chondroitin sulphate (mucopolysaccharide)	Blood clot dissolution
Pig mucosa	Arthrepsin (enzyme)	Rheumatoid Arthritis
Blood	Fibrinolysin (enzyme)	Blood-Clot dissolution
"	Chalones (hormones)	Anti-cancer therapy

GELATIN AND GLUE

Simple processing (e.g. heating with water and dilute acid under pressure) of animal bones and skin gives rise to various grades of gelatins and glues.

Gelatin finds various uses in the food, pharmaceutical and photographic industries. Consumption in the U.S.A. in 1961 was 58,000 lbs.

The yield of glues varies between 10-50% depending on raw materials. Consumption in the U.S.A. in 1965 was 90,000,000 lbs.

DAIRY PRODUCTS

Rennet, or Rennin, a natural enzyme, can be obtained from the 4th stomach of the calf.

Hydrolysis of milk with rennet yields approx. 3% of the phospho protein casein. By acid hydrolysis, or condensation with formaldehyde, casein forms polymers, which find quite wide use as plastics. Casein also finds uses in adhesives, paints and textiles.

Lactic acid may be produced from sour milk, but is best prepared from glucose.

SKEPTIKAL CHYMIST

At present the major sources of many highly useful and valuable organic compounds, ranging from plastics to medicines, are non-renewable hydrocarbons—oil and coal. This article looks at the possibility of obtaining these chemicals on a small scale from *renewable* sources—such as wood and seaweed.

On examination of the present and past processes for the production of chemicals from renewable natural resources, the following significant points emerge:

- *Many of the resources are renewed in a fairly short life-span (1-10 years).*
- *They are often labour, as opposed to capital intensive.*
- *Many processes use only 'waste' by-products of normal production.*
- *Many of the processes are based on pre-industrial techniques; and are thus readily adaptable to the criteria of Alternative Technology.*

Products to which these criteria apply include: *Plant Products:* wood, sugar, starch, natural dyes, insecticides, oils, fats, waxes, cosmetics, cork, drugs, pectins and peat. *Marine Products:* seaweed and drugs. *Animal Products:* drugs, enzymes, gelatin, glue, dairy products (rennet etc).

Space (and personal ignorance) will not permit me to discuss all of these processes. I have therefore chosen three. The first is as yet theoretical, but should become of increasing importance, namely the extraction of *organic chemicals from carbohydrates.* And two others of proven use: *wood* and *seaweed.*

ORGANIC CHEMICALS FROM CARBOHYDRATES

Organic chemicals are very important to humanity today. They supply the starting materials for: plastics, perfumes, drugs, colouring dyes, petrol and other solvents, fats and waxes, and a host of other everyday substances. At the moment the major sources for most of these organic 'building blocks' are petroleum and to a lesser extent coal—both non-renewable.

Up to twenty years ago a significant quantity of chemicals such as ethanol (the alcohol in booze), propanol, acetone and butanol were produced from carbohydrates such as starches, sugars and molasses, but the wide availability of cheap petroleum in the middle 1950's rapidly killed off this more ecologically sound process.

The greatest natural source of energy is the Sun. Plants trap and store the Sun's energy in the form of carbon compounds. These compound carbohydrates are formed from carbon dioxide, water, and trace elements, in a reaction sustained by light and catalysed by chlorophyll, the total reaction being called *photosynthesis.* These carbohydrates occur in a variety of forms (See table below).

Although, in theory, any of the above sources may be utilised, the most promising candidate

A modern still for the distillation of turpentine from Oleoresin developed by the US Naval Stores Station, Olustie, Florida.

would appear to be cellulose, and to a lesser extent starch. Cellulose is the world's major industrial carbohydrate, annual world production being in the region of 100 billion tons (American). Cellulose itself is a rather intractable polymer of glucose units, and the hydrolysis of this polymer (enzymatically or chemically) to glucose would appear to be a necessary step in most schemes making use of it.

The reactions of glucose, of interest to anyone hoping to use it as a starting material for synthesising the organic building blocks which currently come almost exclusively from petroleum, are widely scattered in the chemical and biological literature and require digging out by someone! Until this is done it is impossible to sketch out

Carbohydrates	Sources
Cellulose	Trees, shrubs, plant stalks, grasses, and so on, bacteria.
Starch	Cereals, roots, tubers, pith
Glucose	Starch, honey, grapes, dates
Sugar (Sucrose)	Cane and beet, maple tree
Gums, pectins and mucillages	Trees, fruit of all kinds, seeds
Hemicelluloses and pentosans	Trees, Leafstalk, corn-cobs
Alginates, agars and carrageenans	Sea weeds
Copra and nuts	Coco-nuts, trees
Honey	Bees
Microbial polysaccharides	Bacteria and moulds
Specialist sugars	Fermentation industries, polysaccharides
Biologically active carbohydrates	Animal tissues and fluids, micro-organisms, synthetic compounds

From 'Industrial Uses of Carbohydrates', Maurice Stacey *Chemistry and Industry* pp. 222-226 (1973).

realistic schemes of relatively straightforward syntheses suitable for those who do not have the resources (money and technicians), or desire, to slave away at some complex route. Reactions, such as the aromatisation of glucose to catechol (1, 2-Dihydroxybenzene) are well known and may provide some starting points, (ironically, catechol is one of the few organics readily available from natural resources).

But the most direct way of producing some chemicals may be by reviving some of the earlier fermentation techniques. Ch. Weizmann, the first President of Israel, did pioneering work in this area, and a recent (1974) report from the US National Academy of Sciences suggests that the Americans may also be taking it seriously.

WOOD

Until the middle and late 19th century, when the distillation of coal assumed prominence, the distillation of wood supplied many of the common organic chemicals (especially solvents). As Fig 1 indicates, wood could supply a very wide range of organic chemicals.

Rather than go into further detail on all these processes some of which are fairly complex, I shall select one which illustrates the potential of wood chemistry and which, due to its long tradition, may be of immediate use, namely: wood distillation.

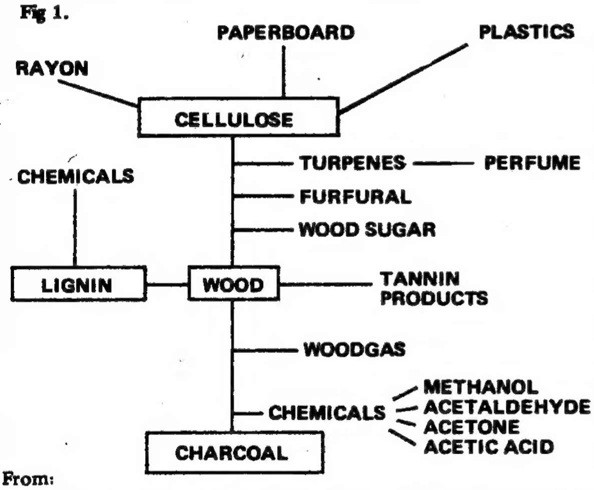
For many thousands of years wood has been used as a fuel and as a source of charcoal for the reduction of ores for their metal content. However, it was not until the beginning of the era of modern chemistry that the real usefulness of all the by-products came to be recognised. By the end of the 17th century it was known that wood burnt in closed vessels produced vapour from which could be condensed a tar and a watery liquid, termed pyroligneous acid. In 1658 Glauber identified the main product of this distillation as acetic acid (vinegar), and Boyle, in his *Sceptical Chemist* (1661), noted the presence of an inflammable volatile liquid, 'wood spirit', later named methyl alcohol, signifying the wine of wood. However, it was not until the Frenchman Lebon, in 1799, took out a patent for, "a new method of employing fuel more efficiently, for heating or lighting, and of collecting the various products" (soon all Paris was to admire his gas-lamp in the Hotel Seignelay), that things really got going.

The basic details of the process are given in Fig 2.

Fig 3 shows the section of a battery of retorts *(A)* of the Mathieu type. The wood is charged automatically from the running buckets, *(c)*, suspended at *g*. At the end of the operation the charcoal is discharged into the vessel, *(P)*, which is provided with a cover to prevent the hot charcoal from igniting in the air. The vapours from the distillation pass into the tube, *(H)*; which conducts them into a coil cooled by the water in *T* and then into the barrel, *(J)*, where the tar and the pyroligneous acid separate; the gas, which does not condense, but is still partly combustible, is washed and passes through the pipe, *(k)*, to be burnt under the furnace-hearth, *(D)*; there is no danger of explosion, since, if there is any air in the retorts, it cannot communicate with the hearth, the barrel, *(J)*, serving as a water-seal.

The products obtainable from a typical dry distillation operation are as shown in Fig 4. See overleaf.

Fig 1.



From:
'Chemicals from Biological Resources' Alan J.P. Dalton *ITDG*(1973)

Fig 2. Products of wood distillation

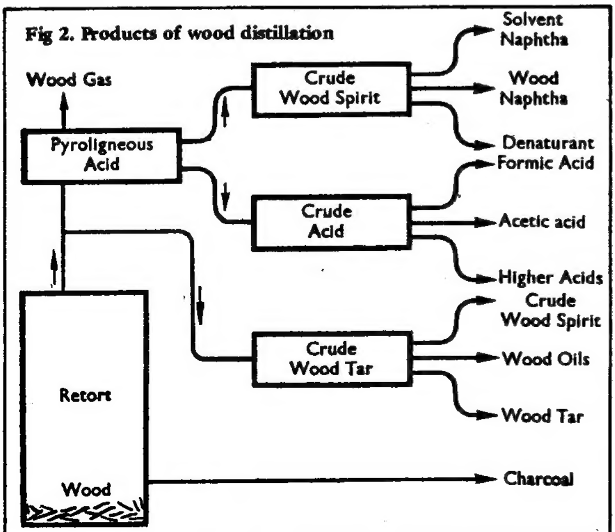
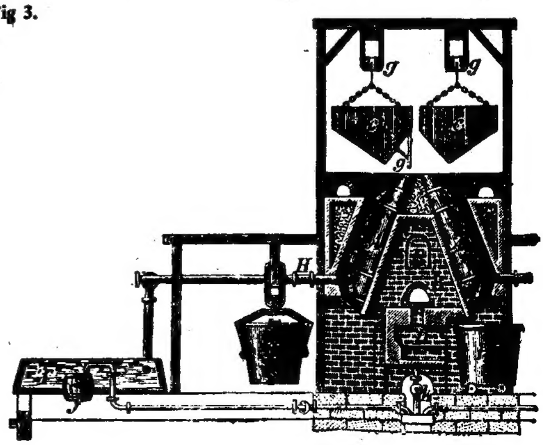


Fig 3.



Source: *Molimasis's Chemistry* Vol 2, pt 1, J.A. Churchill (1921).

Fig 4.
Products obtained by dry-distillation of 1 ton of hardwood scrap (ca. 70% maple, 25% birch, 5% ash, elm and oak)

Charcoal	600 lb
Gases:	5,000 cu ft
Carbon dioxide (38%)	
Carbon monoxide (23%)	
Methane (17%)	
Nitrogen (16%)	
Methanol	3 gall
Ethyl acetate	15 gall
Ethyl formate	1.3 gall
Acetone	0.7 gall
Creosote oil	3.3 gall
Sol. tar	22 gall
Pitch	66 lb

Source: Alan J.P. Dalton, 'Chemicals from Biological Resources' *ITDG*, (1973).

SEAWEED

From the 17th century until the development of the Le Blanc process, in 1781, seaweeds formed the major source of alkali (sodium and potassium carbonates) in Europe, their ash being known in Scotland and Ireland as 'kelp'. From then until the 1930's there was a lull in the industry, but from then on increasing use was found for one of the major products: Alginic acid. Figs 5-8 give some idea of the products available from seaweed; the earlier manufacture of soda and iodine; the three major products of the industry; the organic chemicals (sugars and steroids) that have been produced by simple laboratory procedures; and the occurrence of seaweeds throughout the world.

Harvesting seaweed off the coast of Australia

The giant kelp ***Macrocystis pyrifera***

Fig 5.

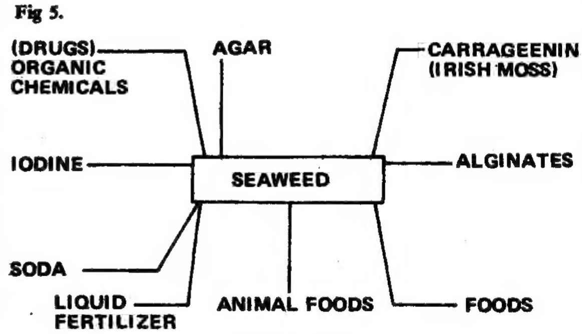
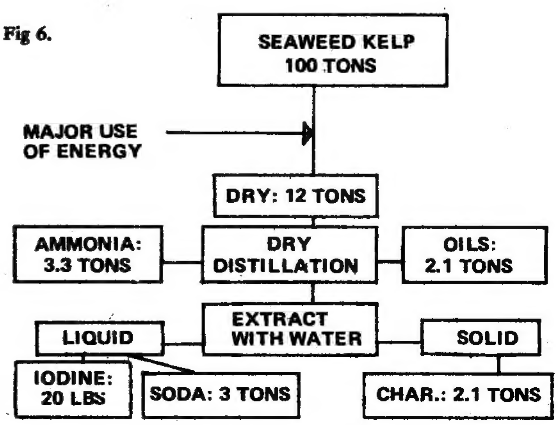


Fig 6.



From:
'Chemicals from Biological Resources' Alan J.P. Dalton *ITDG* (1973)

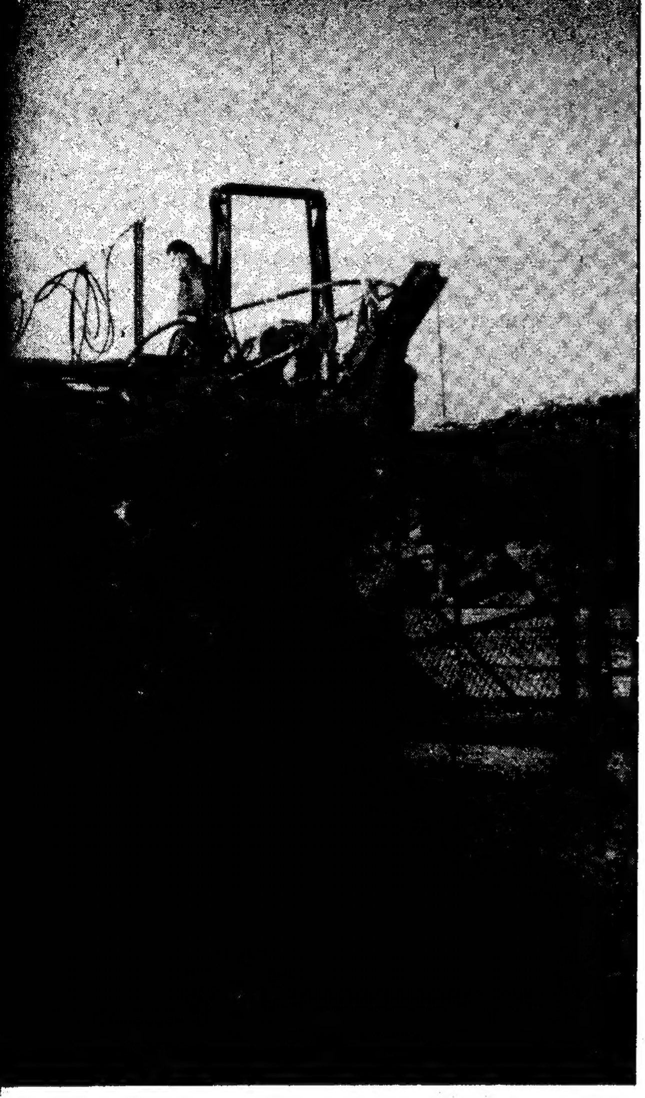


Fig 7.

Chemicals potentially available per annum from 1,000 tons of fresh 'L. Cloustini' (whole plant)

Chemical	*Calculated tonnage present in weed*		
	May	October	Average
Alginic acid	28	31	30
Mannitol	10	33	18
Laminarin	Nil	40	14
Fucoidin	6	9	7.5

Source: *Organic Chemistry Today* F.W. Gibb, Penguin (1964).

Fig 8.

Product	Uses
Agar	Microbiology Foodstuffs Pharmaceuticals
Alginates	Pharmaceuticals Foods Rubber Textiles Paper
Carrageenin	Largely foodstuffs Ceramics Alcoholic drinks Electroplating Leather finishing

Source:
Alan J.P. Dalton, 'Chemicals from Biological Resources' *ITDG*, (1973).

It would appear that much Scottish and Irish seaweed is still gathered by hand—which cannot be much fun on a rainswept and windy beach at the height of winter. The processes for the extraction of these chemicals have been developed by the now defunct Scottish Seaweed Research Institute, during the 1950's, and may well have been improved on by now. The original methods were simple and admirably suited for communities located near large amounts of seaweed; for most practical purposes the North West coast of Scotland and the West coast of Ireland.

Incidentally, it is possible to cultivate seaweed (the red seaweed, *Porphyra tenera,* has been cultivated for food in Japan for years), but the problem of interference to shipping and fishing, coupled with the major changes in the environment which would occur as a result, led to the dropping of such proposals from the British industry, under pressure from the Ministry. Anyone familiar with the apparently uncontrollable growth of red seaweed now going on along Britain's south coast, will understand the need for caution. In short, the problems may well be social and ecological rather than technical.

Alan Dalton

Part of an alginate producing plant in Scotland

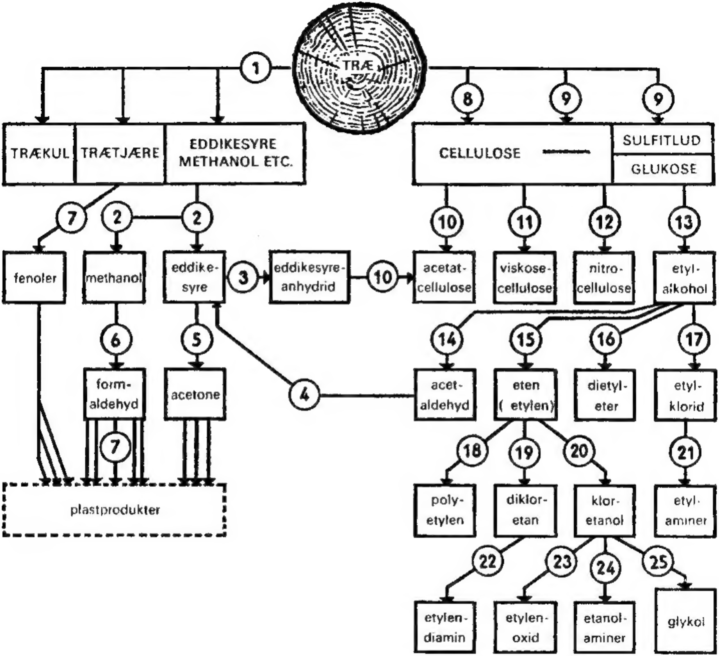


Fig. 6 Skema over trækemiens muligheder. Det ses, at en masse forskellige produkter kan fremstilles af træ. Figuren er taget fra „Boken om Naturen“, Bokförlaget Forum, Stockholm 1952, s. 222.